Ultramicroscopy 156 (2015) 18–22

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

Novel sample preparation for operando TEM of catalysts

Benjamin K. Miller [a], Trevor M. Barker [a], Peter A. Crozier [a,*]

[a] School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ 85287-6106 USA

ARTICLE INFO

Article history:
Received 19 November 2014
Received in revised form
27 April 2015
Accepted 4 May 2015
Available online 5 May 2015

Keywords:
Operando
In-situ TEM
Environmental TEM (ETEM)
TEM sample
EELS
Catalyst

ABSTRACT

A new TEM sample preparation method is developed to facilitate *operando* TEM of gas phase catalysis. A porous Pyrex-fiber pellet TEM sample was produced, allowing a comparatively large amount of catalyst to be loaded into a standard Gatan furnace-type tantalum heating holder. The increased amount of catalyst present inside the environmental TEM allows quantitative determination of the gas phase products of a catalytic reaction performed *in-situ* at elevated temperatures. The product gas concentration was monitored using both electron energy loss spectroscopy (EELS) and residual gas analysis (RGA). Imaging of catalyst particles dispersed over the pellet at atomic resolution is challenging, due to charging of the insulating glass fibers. To overcome this limitation, a metal grid is placed into the holder in addition to the pellet, allowing catalyst particles dispersed over the grid to be imaged, while particles in the pellet, which are assumed to experience identical conditions, contribute to the overall catalytic conversion inside the environmental TEM cell. The gas within the cell is determined to be well-mixed, making this assumption reasonable.

1. Introduction

Linking catalyst microstructure to catalytic performance is a primary objective to advance the science of heterogeneous catalysis. To accomplish this, one must know the structure of a working catalyst when it is catalyzing a reaction of interest. Various methods have been applied to determine this structure using transmission electron microscopy (TEM). High surface area catalysts can be studied in the TEM, then used in a reactor and, after reaction, again observed in the microscope [1,2]. This post-mortem analysis can yield important information, but may not reveal the structures present during the reaction, as these may be transient, and exist only under reaction-conditions [3,4]. *In-situ* techniques attempt to solve this problem by imaging the sample while subjecting it to conditions that simulate a reactor [5,6]. This is a powerful technique, and many advances have been made recently allowing higher pressures over 1 atm [7,8], as well as rapid heating with minimal thermal drift of the sample [9,10].

Despite these advances, the conditions within the microscope are still often different from conditions present in *ex-situ* reactors. Additionally, the temperature and gas composition inside the ETEM cell are sometimes not accurately known [11,12]. If the conditions are not precisely known or controlled, a catalyst which may be assumed to be active may actually be inactive and the link between catalyst structure and performance will be ambiguous. To address this problem it is necessary to measure the catalyst's relative activity throughout the *in-situ* experiment. This is the goal of *operando* TEM. In an *operando* experiment, the gas composition within the microscope is measured [13,14]. This decreases the uncertainty regarding the gas composition around the sample. More importantly, it makes it possible to follow the course of the reaction, monitoring the changes in catalyst activity and structure simultaneously. Now the ensemble of structures observed in the TEM is unambiguously active for the reaction being studied whenever the expected gaseous products are observed. The correlation between the relative catalyst activity and the catalyst structure will now be much tighter.

A traditional TEM sample has a very low surface area over which to disperse a catalyst powder, and the minute amount of catalyst inside the microscope will yield a correspondingly small number of product gas molecules. In a windowed cell setup, it may be possible to detect this small number of product gas molecules in the outlet flow from the holder, since the total flow is quite small [15]. In a differentially pumped environmental TEM (ETEM) [12] however, the reactant-gas flow is much larger, so the partial pressures of product gases will be smaller. If these partial pressures are near the detection limit of the equipment used to measure the gas composition, it will be difficult to accurately measure the catalyst's changing activity. A simple solution to this problem is to increase the amount of catalyst present in the TEM, so that an

* Correspondence to: Engineering G Wing, #301, 501 E. Tyler Mall,Tempe, AZ 85287-6106, USA. Fax: +1 480 727 9321.
E-mail address: crozier@asu.edu (P.A. Crozier).

http://dx.doi.org/10.1016/j.ultramic.2015.05.003
0304-3991/

easily quantifiable amount of product gas is produced. This paper describes a new sample preparation technique to achieve this increase for a differentially pumped ETEM.

2. Materials/methods

2.1. Operando sample preparation

The TEM sample developed for *operando* TEM is a combination of two distinct samples, simultaneously loaded into a single TEM holder, as depicted in Fig. 1. The first part of the sample is a metal mesh grid over which a catalyst is dispersed.

The second half of the sample is an inert porous *operando* sample pellet, made from Pyrex glass fibers, which is also covered with the same catalyst (CO conversion on the Pyrex and mesh was shown to be neglible). The TEM holder for which this sample was created is a Gatan furnace-style heating holder. This holder supports a standard 3 mm TEM sample inside a small furnace. A hex ring with exterior threads screws into the internally threaded furnace body, securing the sample in place. Both the grid and pellet must fit into this 0.75 mm deep furnace.

To produce the *operando* sample pellet, Pyrex fibers (about 80 μm in diameter) are first crushed in a small mortar and pestle so that the length of each fiber is on the order of a millimeter. This prevents self-alignment of fiber bundles, which was found to occur with long, uncrushed fibers. The crushed fibers are then packed into a 3 cm long quartz tube whose inner diameter is 3 mm. The packed tube is then fired at 700 °C for 3 h, to initiate sintering of the fibers into a network. After cooling to room temperature, the resulting porous cylinder of networked fibers is pushed out of the quartz tube, and sliced into sections approximately 1–2 mm thick with a razor blade. One side of each section is ground flat with sandpaper before placing the section into a small jig designed for finishing the pellets. The jig, depicted in Fig. 2c, consists of two steel parts with a 0.8 mm hole through the centers. One of the parts has a counter bore that is 0.6 mm deep to accommodate the pellet. The pellet is placed, flat surface down inside this counter bore, and the rough surface is ground to the level of the steel with sand paper, leaving a 0.6 mm thick pellet. The steel pieces are then put together, and a 0.8 mm drill bit bores a hole through the pellet, guided by the steel parts to the exact center. The finished pellet is rinsed on a filter paper with nano-pure water to flush out any residual loose fibers. Loading catalyst onto the porous pellet is accomplished by impregnation using a suspension of the catalyst in water (see Fig. 2b). Single drops of this catalyst suspension are impregnated into the pellet and allowed to dry before the next drop is added. The pellets are kept at about 80 °C during this process to decrease the drying time between drops. The loading

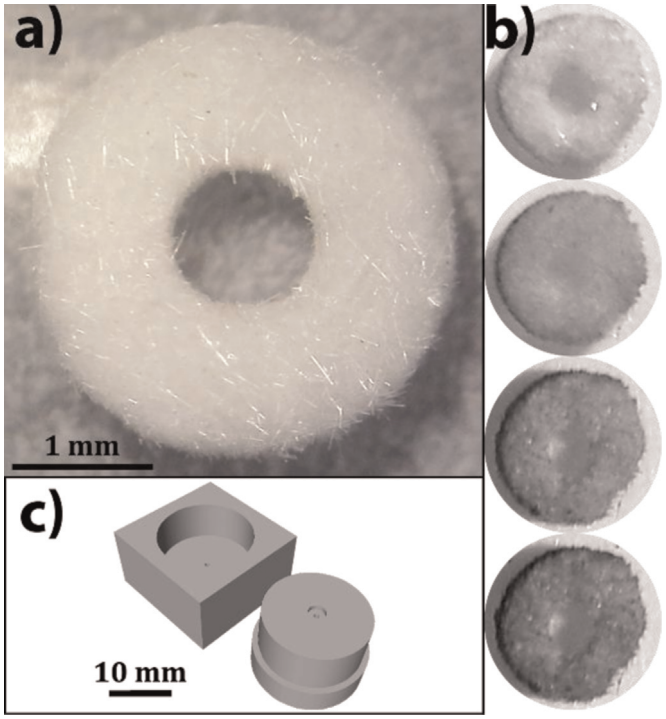

Fig. 2. Operando Pellet. (a) Optical images of the operando pellet, showing the texture and size. The hole in the center allows the electron beam to pass, and the wire mesh grid to be observed in the TEM. (b) Series of images of an operando pellet after successive drops of a catalyst suspension have dried. (c) The jig designed to finish the pellets, showing the small counter bore, in which the pellet sits, in the right half.

can be varied as needed, but for the present work was on the order of 5 μg of supported catalyst per pellet.

An *operando* pellet produced by the method just described is seen in Fig. 2a. The pellets are approximately 3 mm in diameter and 0.6 mm thick, and weigh approximately 3 mg each, though there is some variation from one pellet to the next. The hole in the pellet is large enough that it does not place any additional restrictions on the maximum tilt angle achievable using the holder which is 35°. A typical pyrex pellet has a porosity of about 70%, and thus good gas permeability. A typical pyrex pellet also has a large surface area, which can be calculated by considering that the pellet is composed of cylindrical fibers of known density. The surface area of a cylinder (neglecting the end caps) is $2\pi rL$, while the mass of the cylinder is $\pi r^2 \rho L$. Combining these two equations yields the surface area in terms of the mass, fiber radius, and density. This approach gives a surface area of approximately 7 cm^2 (0.2 m^2/g)

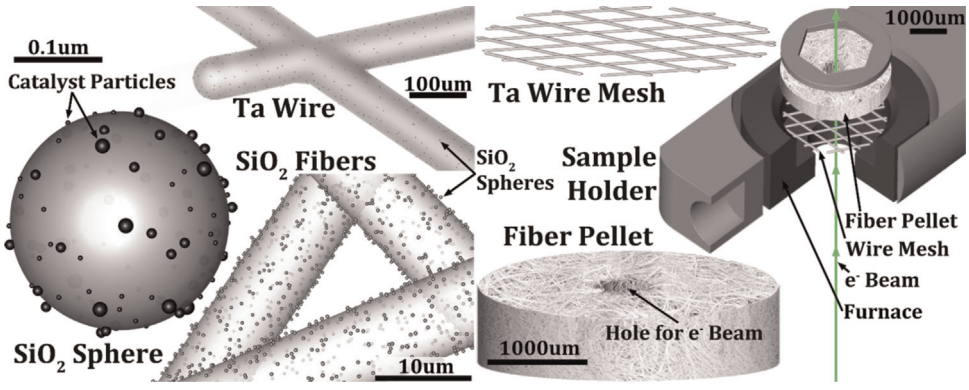

Fig. 1. Operando TEM sample. An overview of the sample configuration used in the operando experiments. Both a Ta wire mesh and a SiO_2 fiber pellet are covered with silica-sphere-supported Ru catalyst particles, and placed inside the holder, with the wire mesh closer to the eucentric plane in the Ta heating holder.